

[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

A Study of the Nitrate Ion Dissociation in Fused Nitrates¹

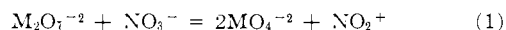
BY ROGER N. KUST AND F. R. DUKE

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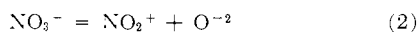
In fused alkali nitrates the nitrate ion dissociates according to the reaction $\text{NO}_3^- \rightleftharpoons \text{NO}_2^+ + \text{O}^{2-}$. The equilibrium constant K_1 for the dissociation was determined potentiometrically in a fused equimolar NaNO_3 - KNO_3 solvent. An oxygen-platinum electrode was found to be reversible to the oxide ion; a silver-silver nitrate (1.0 *m* AgNO_3 in equimolar NaNO_3 - KNO_3 solvent) electrode in a glass envelope was used for the reference electrode. The nitryl ion was added through the equilibrium: $\text{S}_2\text{O}_7^{2-} + \text{NO}_3^- = \text{NO}_2^+ + \text{SO}_4^{2-}$, while various oxide ion concentrations were obtained coulometrically. At 250°, $K_1 = 2.7 \pm 0.3 \times 10^{-26}$ and at 300°, $K_1 = 5.7 \pm 0.1 \times 10^{-24}$; ΔH° and ΔG° (kcal., 250°) are 63.3 and 60.9, respectively, and ΔS° is 4.6 e.u. (cal. deg.⁻¹).

Introduction

The addition of an oxide ion acceptor, such as the pyrosulfate anion, to fused alkali nitrates apparently results in the production of nitryl ion, according to the reaction^{2,3}



This suggests that there should be an equilibrium of the sort



quite analogous to the self-dissociation of water. This paper is a report on the electrochemical determination of this self-dissociation constant for nitrate ion in a fused equimolar mixture of sodium and potassium nitrates.

Experimental

All chemicals used were of reagent grade. The solvent of equimolar sodium-potassium nitrates was prepared by fusing the proper proportions of the two salts, mixing well, filtering through a fine grade fritted glass disk, and molding into slugs of about 100 g. All reagents were dried at 110° and were stored over magnesium perchlorate.

The reaction vessel was similar in design to that used by Duke and Garfinkel.⁴ The oxygen gas electrode consisted of a 0.5 cm.² piece of platinized platinum over which O_2 was bubbled. The reference electrode used in conjunction with the oxygen gas electrode consisted of a silver wire dipping into a 1.0 molal solution of silver nitrate in equimolar (Na,K)NO₃ solvent. This was contained in a Pyrex tube, the end of which was blown to a thin membrane. This Pyrex tube then dipped into the reaction mixture.

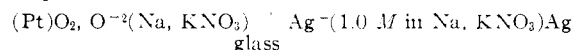
In the determination of the standard e.m.f. of the electrochemical cell, the oxygen pressure was varied by dilution with argon. The flow rates of the argon and oxygen were measured before mixing with *n*-butyl phthalate manometers. These manometers were calibrated with a gas buret and by direct displacement of water. After passing through the flowmeters, the two gases were mixed. Adequate mixing was attained by passing the mixed gases through a Pyrex spiral made from 6 ft. of 5-mm. Pyrex tubing. Oxide ion was introduced into the equimolar solvent through electrolysis. This was done by reducing oxygen gas at the platinized platinum electrode. During the electrolysis the reference electrode previously described was replaced by an electrode of similar composition but which had an asbestos wick salt bridge in place of the glass membrane. This change lowered the internal resistance of the cell. Currents of 2 to 20 μa . were obtained from a constant current generator. The voltage across the cell during electrolysis varied from 0.03 to 0.05 v. After each electrolysis, the asbestos wick electrode was replaced by the glass membrane reference electrode. All e.m.f. measurements were made against the glass membrane reference electrode.

Potential measurements were made with a Leeds and Northrup K-3 universal potentiometer. A Keithley Model 603 electrometer-amplifier was connected in series with the unknown potential and was used as a null indicator. The input impedance of the electrometer was set at 10¹¹ ohms.

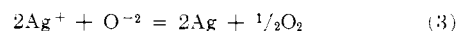
Results and Discussion

An oxygen electrode was developed which, in conjunction with the silver-silver nitrate reference electrode previously described, would indicate oxide ion

concentration. The electrochemical cell for this electrode pair can be indicated



and the cell reaction can be written



The reversibility of this cell was demonstrated and the standard e.m.f. for the cell reaction was obtained by varying the oxygen pressure and the oxide ion concentration independently.

In the experiments in which the oxygen pressure was varied by dilution with argon, small amounts of a base were added in order to increase the over-all oxide ion concentration. Sodium orthosilicate was used as the base because it formed no gaseous products. Figure 1 is a plot of e.m.f. vs. log *P* for a typical experiment at 250°. In this instance the orthosilicate concentration was $1.74 \times 10^{-4} \text{ M}$. The theoretical Nernst slope for a 4-electron process at 250° is -0.0260 v. The observed slope, obtained from a least squares analysis, was $-0.0276 \pm 0.0008 \text{ v}$.

In the experiments in which the oxide ion concentration was varied, the oxide ion was introduced electrolytically as previously described. The oxygen pressure was maintained at atmospheric pressure and all potential measurements were corrected to an oxygen pressure of 1 atmosphere. The results obtained for three different oxygen electrodes at 273° are shown in Fig. 2. The theoretical Nernst slope under these conditions is 0.0541 v. The observed slope was $0.0543 \pm 0.0013 \text{ v}$. The variation of the standard e.m.f. with temperature is shown in Fig. 3. The values of ΔG° , ΔH° , ΔS° at 273° for the cell reaction, eq. 3, are listed in Table I.

TABLE I
VALUES OF ΔG° , ΔH° , ΔS° FOR THE CELL REACTION

Solvent	<i>T</i> , °C.	ΔG° , kcal.	ΔH° , kcal.	ΔS° , e.u.
Equimolar (Na,K)-NO ₃	273	-29.5 ± 0.1	-35.9 ± 0.3	-11.8 ± 0.4
Pure NaNO ₃	323	28.9 ± 0.1	-35.5 ± 0.4	-11.0 ± 0.7

Several workers^{5,6} have shown that the sodium-potassium cation ratio effects the rate and equilibrium constants of several reactions which were carried out in sodium-potassium nitrate solvents. Therefore it seemed advisable to ascertain the effects of the cation ratio on the standard e.m.f. of the cell. To accomplish this, a solvent of pure sodium nitrate was substituted for the equimolar solvent. The electrolysis experiment was repeated and the standard e.m.f. and its temperature dependence were determined. The value of the standard e.m.f. at 323° is $0.6264 \pm 0.0002 \text{ v}$. The temperature dependence is shown in Fig. 3 and the

(1) Contribution No. 1302. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) F. R. Duke and M. L. Iverson, *J. Am. Chem. Soc.*, **80**, 5061 (1958).

(3) F. R. Duke and S. Yamamoto, *ibid.*, **81**, 6378 (1959).

(4) F. R. Duke and H. Garfinkel, *J. Phys. Chem.*, **65**, 461 (1961).

(5) F. R. Duke and J. M. Schlegel, to be published.

(6) F. R. Duke and E. A. Shute, *J. Phys. Chem.*, **66**, 2114 (1962).

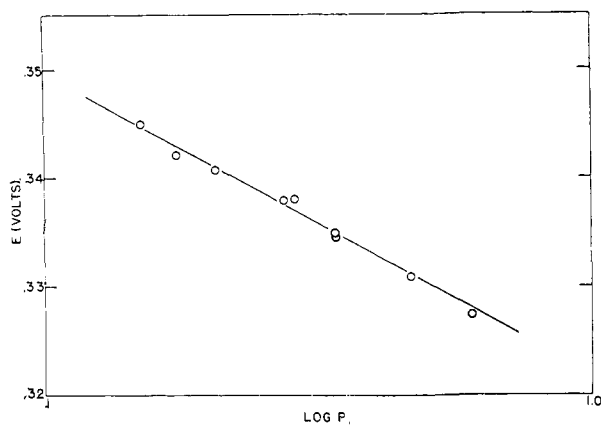


Fig. 1.—Plot of E vs. $\log P_{O_2}$ at 250° to determine reversibility of electrode system.

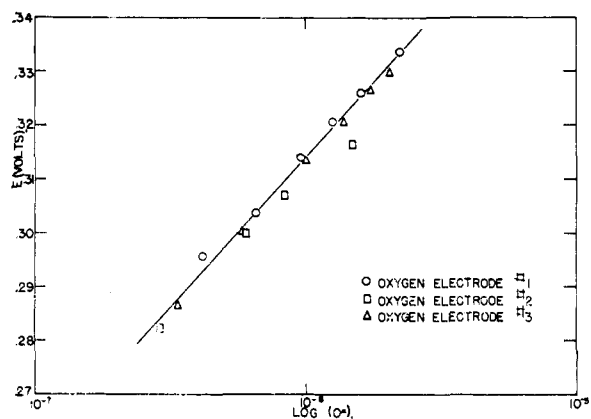


Fig. 2.—Plot of E vs. $\log (O^{2-})$ at 273° for three different electrodes to determine reversibility and reproducibility of the electrode system.

values of ΔG° , ΔH° , ΔS° are listed in Table I. Comparison of the ΔG° values in the two solvents indicates that there is a small cation effect on the cell reaction.

Nitrate Ion Dissociation.—If the nitrate ion dissociates according to reaction 2, then in a nitrate solvent the equilibrium constant can be written

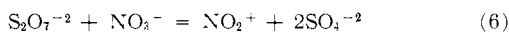
$$K_1 = (NO_2^+)(O^{2-}) \quad (4)$$

If the concentration of the oxide ion is eliminated from the Nernst expression for the electrochemical cell, eq. 3, with eq. 4, the equation

$$E = E^\circ - \frac{RT}{2F} \ln \frac{(P_{O_2})^{1/2}(NO_2^+)}{K_1} \quad (5)$$

is obtained.

In the presence of the pyrosulfate anion, the equilibrium



is established,³ which has the equilibrium constant

$$K_2 = (NO_2^+)(SO_4^{2-})^2 / (S_2O_7^{2-}) \quad (7)$$

It has been shown³ that the rate of decomposition of the pyrosulfate anion is proportional to the concentration of the total acidity, T_a , which is defined as

$$T_a = (S_2O_7^{2-}) + (NO_2^+) \quad (8)$$

If the pyrosulfate concentration is eliminated from eq. 7 and 8, and if the nityl ion concentration is eliminated from this result and eq. 5, the following expression is obtained

$$E = E^\circ - \frac{RT}{2F} \ln \frac{(P_{O_2})^{1/2} T_a}{K_1 \left[1 + \frac{(SO_4^{2-})^2}{K_2} \right]} \quad (9)$$

Therefore K_1 can be determined from a measurement of E and T_a at a known oxygen pressure, a known value of

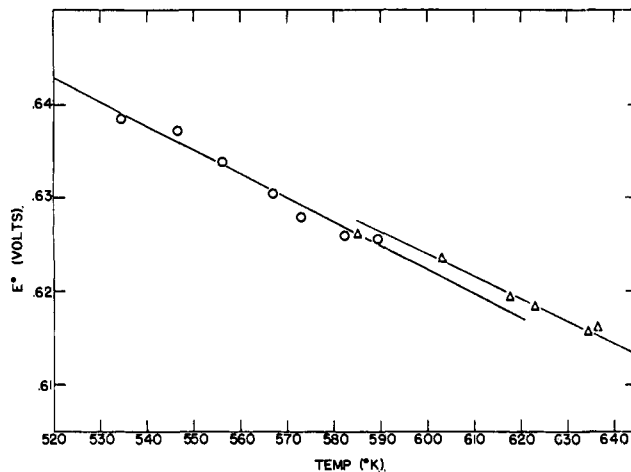


Fig. 3.—Plot of E° vs. absolute temperature to determine ΔH° of electrode reaction in: O, equimolar sodium-potassium nitrate; Δ , pure sodium nitrate.

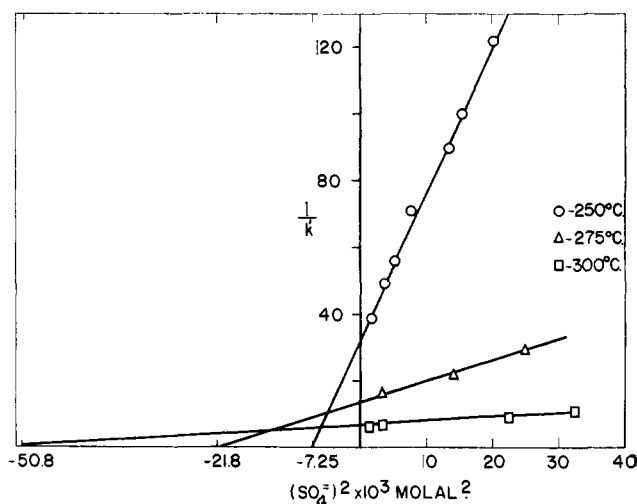


Fig. 4.—Plot of reciprocal rate data vs. $(SO_4^{2-})^2$ to determine k and K at 250, 275, 300°.

K_2 , and a sulfate ion concentration sufficiently large so that the additional sulfate produced from the pyrosulfate decomposition will be small in comparison.

Duke and Yamamoto³ have determined the constant K_2 for reaction 6 by following the kinetics of the pyrosulfate decomposition. Because of the relatively large probable errors in their data, it seemed advisable to redetermine K_2 following the kinetics with the oxygen electrode. It might be expected that this physical method would be more accurate than the chemical method used by these workers.

The rate expression developed by Duke and Yamamoto is

$$-\frac{dT_a}{dt} = \frac{kK_2T_a}{K_2 + (SO_4^{2-})^2} = k'T_a \quad (10)$$

where k is the specific rate constant, K_2 is the equilibrium constant for reaction 6, and k' is a pseudo-first-order rate constant. Since the oxide ion concentration is inversely proportional to the total acidity, the potential of the oxygen-silver electrode system should be a linear function of $\ln T_a$. Therefore a plot of potential vs. time should be a straight line with a slope equal to $RTk'/2F$.

Pseudo-first-order rate constants were determined at 250, 275, and 300° for known sulfate ion concentrations. The values of the reciprocals of the pseudo-rate constants at each temperature were plotted against the square of the sulfate ion concentration. The results are shown in Fig. 4. The ordinate intercepts are the

reciprocals of the specific rate constants. The equilibrium constants are the negatives of the abscissa intercepts. The equilibrium constants can also be calculated by dividing the ordinate intercepts, $1/k$, by the slopes, $1/kK_2$. The values of K_2 and k obtained for the three temperatures are listed in Table II.

TABLE II

SPECIFIC RATE AND EQUILIBRIUM CONSTANTS FOR THE PYRO-SULFATE DECOMPOSITION IN EQUIMOLAR (Na,K)NO₃

T, °C.	k × 10 ³ , min. ⁻¹	K × 10 ³ , ref. 3	K × 10 ³ , this study
250	31 ± 6	26	7.2 ± 0.7
275	74 ± 3		21.8 ± .2
300	162 ± 1		50.8 ± .1

The concentration of total acid, T_a , present at any time was determined by an iodometric titration.³ Six or seven samples were taken at each of two temperatures, 250 and 300°, and the corresponding potentials recorded. The constant K_1 was determined from each sample with the aid of eq. 9. At both temperatures it was observed that the dissociation constant K_1 increased with time. This increase can probably be explained by taking into account the increase in sulfate ion concentration which had been assumed to be constant in the derivation of eq. 9. Since the sulfate ion concentration was known accurately initially, the data at each temperature were extrapolated back to zero time. The experimentally determined values of K_1 are listed in Table III. The values of K_1 at zero time are

$$K_1(250^\circ) = (2.7 \pm 0.3) \times 10^{-26}$$

$$K_1(300^\circ) = (5.7 \pm 0.1) \times 10^{-24}$$

If the assumption is made that the enthalpy of dissociation is constant over the temperature range 250–300°, the enthalpy of dissociation can be calculated from the Clausius–Clapeyron equation. The ΔH° value thus obtained and the ΔG° and ΔS° values for the nitrate ion dissociation are given in Table IV.

TABLE III
VARIATION OF K_1 WITH TIME

T, °C.	$K_1 \times 10^{27}$	T, °C.	$K_1 \times 10^{23}$
250	60 min.	300	6 min.
	75 min.		10 min.
	90 min.		16 min.
	105 min.		25 min.
	4 hr.		30 min.
	5 hr.		38 min.
6 hr.	10.40		11.91

TABLE IV

VALUES OF ΔH° , ΔG° , AND ΔS° FOR THE NITRATE ION DISSOCIATION

T, °C.	ΔG° , kcal.	ΔH° , kcal.	ΔS° , e.u.
250	60.9	63.3	4.6
275			
300	60.6		4.7

No mention has been made as to what form the oxide ion takes when in solution in fused nitrates. The measurements so far involved only require the oxide ion to exist as such on the electrode surface and an equilibrium between the oxide ion and any solvated species. It seems reasonable that in a solution of alkali nitrates the oxide ion could exist in forms containing Na⁺, K⁺, or NO₃⁻. The existence of an orthonitrate ion, NO₄⁻³, has been postulated by several workers, among the more recent of which is Kohlmüller,⁷ who prepared both sodium and potassium orthonitrates by dissolving alkali oxides in alkali nitrates. It may be that the orthonitrate ion can exist in solution in alkali nitrate solvents, at least in small concentrations. However, a spectroscopic analysis of such a solution would be needed to establish unequivocally the existence of the orthonitrate ion.

(7) R. Kohlmüller, *Ann. chim. (Paris)*, **4**, 1183 (1959).

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, AMERICAN OIL CO., WHITING, IND.]

Organic Ions in the Gas Phase. XIII. Cycloheptatriene-7-*d*; Decomposition of C₇H₈⁺ and C₇H₈⁺⁺ from Cycloheptatriene and Toluene

BY SEYMOUR MEYERSON

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The mass spectra of cycloheptatriene unlabeled and -7-*d* show that, as in other C₇H₈ isomers, the eight hydrogen atoms lose positional identity in nearly all the decomposition reactions of singly ionized molecules produced by electron impact. Such loss of identity occurs also in decomposition of doubly ionized cycloheptatriene to C₇H₇⁺⁺ and to C₇H₈⁺⁺ and of doubly ionized toluene to C₇H₈⁺⁺, but, in the process whereby doubly ionized toluene loses a hydrogen atom to form C₇H₇⁺⁺, any one hydrogen in the methyl group is about four times as likely to be lost as one in the ring. Thus the distinction between methyl and ring hydrogens survives in the excited doubly ionized state or states involved.

Loss of a hydrogen atom from toluene under electron impact—to give a C₇H₇⁺ ion that most probably has the symmetrical tropylium structure^{1,2}—is preceded or accompanied by a rearrangement in which the eight hydrogen atoms lose identity, as shown by the mass spectra of variously deuterated species of toluene.^{1,2} The questions raised by this finding transcend the toluene system in which they originated. Eight other C₇H₈ isomers have been subjected to electron impact in a mass spectrometer: cycloheptatriene-1,3,5,²⁻⁴ bicyclo-

[2.2.1]heptadiene-2,5,^{2,4,5} spiro[2.4]heptadiene-1,3,^{2,4,6} 1-ethinylcyclopentene,^{2,4} 3-ethinylcyclopentene,^{2,7} methylfulvene,⁸ quadricyclene,⁸ and heptadiyne-1,6.⁹ All of them have spectra remarkably similar to that of toluene. Moreover, the two ethinylcyclopentenenes have

(3) S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957).

(4) V. Hanuš and Z. Dolejšek, *Kernenergie*, **3**, 836 (1960).

(5) S. Meyerson, J. D. McCollum, and P. N. Rylander, *J. Am. Chem. Soc.*, **83**, 1401 (1961).

(6) V. Hanuš, *Nature*, **184**, 1796 (1959).

(7) V. Hanuš and Z. Dolejšek, *Jaderná energie*, **6**, 350 (1960).

(8) V. Hanuš and Z. Dolejšek, *Collection Czechoslov. Chem. Commun.*, **28**, 652 (1963); Z. Dolejšek, V. Hanuš, and H. Prinzbach, *Angew. Chem.*, **74**, 902 (1962).

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(2) H. M. Grubb and S. Meyerson, in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, Inc., New York, N. Y., 1963, p. 453.